



Facile hydrophobic modification strategy on hydrophilic metal organic frameworks for improved toluene capture.

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1 Introduction

Until now, adsorption by porous materials is the most demonstrated technology used for VOCs abatement. Standard air cleaning devices/filters contain carbon-based sorbents given their low cost, high porosity, and stability. Despite these advantages, they are known as structurally amorphous. The scarcity of precise structural details restricts further optimization studies for enhanced adsorptive performance (Xie *et al.*, 2018). Recently, intense research is concerted on a superior class of adsorbent known as metal-organic frameworks (MOFs); built from metal ions bridged with organic linkers. MOFs are characterized with orderly pore structure, high surface area, versatile reusability, and functionalities for vast application prospects particularly in the field of volatile organic compounds (VOCs) treatment (Wang *et al.*, 2019). However, to achieve effective VOCs removal even with the ubiquitous moisture presence, the material needs to feature high water resistance and surface area. Therefore, realizing the limitations from conventional carbon sorbents and the harms posed by VOCs in our surrounding, it is increasingly relevant to

focus on developing water-stable MOFs as a potential alternative. By starting with a hydrophilic and highly porous MOF (MIL-100), this study explores the effects on the toluene capture performance after a facile surface modification treatment using alkyl phosphonic acids.

2 Materials/Methods

Materials: 1-Decylphosphonic acid (DPA, 98%), n-octadecylphosphonic acid (97%, ODP) and iron chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were procured from Alfa Aesar. Trimesic acid (H_3BTC) was supplied by Sigma-Aldrich. All solvents and chemicals were from reagent grade and used without further purification.

Methods: The synthesis of MIL-100 follows a sustainable preparation method described previously (Guesh *et al.*, 2017) where Solution 1 was first prepared by mixing 1.7 g H_3BTC (7.6 mmol) with 1 M NaOH solution (22.8 mmol). Solution 2 contains 2.26 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (11.4 mmol) fully dissolved in 97.2 g of deionized water. Next, Solution 1 was added dropwise to Solution 2 at room temperature and left stirred

for 24 hours. The resultant solid powder was washed thrice with water and last rinse using ethanol before dried at room temperature. The surface modification protocol was done according to a previous literature (Sun *et al.*, 2017). About 0.05 g of dried MIL-100 powder was soaked in 50 mL of 5 mM OPA/ethanol solution (likewise for ODPA) for 24 hours at ambient condition. After the set period, the solution was filtered, and the filtrate was washed thrice with ethanol. The modified products (MIL-100-OPA and ODPA) were then evacuated for 24 hours at 120 °C. The accessible porosity of the tested materials was probed using N₂ gas adsorption at 77 K on Micrometrics 3Flex Surface Analyzer. Toluene vapor adsorption isotherms of toluene were measured in Dynamic Vapor Sorption (Endeavour, Surface Measurement Systems) instrument at 303 K at 95% P/P₀.

3 Results and Discussion

The preliminary toluene adsorption experiment (Figure 1) reveals comparatively high toluene adsorption capacity by MIL-100-DPA (458 mg/g) and MIL-100-ODPA (474 mg/g) with respect to the pristine form (582 mg/g). These promising uptakes altogether exceeded more than double compared to that of a commercial activated carbon (~250 mg/g) (Hunter-Sellars *et al.*, 2020). Minimal changes observed on the pore volume and the surface area after the modification further support the utility of this approach without compromising the interior access much (Table 1). The pore size distribution analysis of the samples confirms the presence of broad meso and macropores which presumably contribute to the high toluene uptake. In terms of the adsorption mechanism, although MIL-100 contains Fe metal centres acting as strong Lewis acid sites (electron-pair acceptor), the toluene molecules tend to distribute favourably around the proximity of the ligands (Duan *et al.*, 2019). This phenomenon is consistently observed even at higher toluene vapor pressure, suggesting there is a strong π - π conjugate stacking interaction formed between the toluene and the ligand.

Table 1. BET surface area analysis of the MOFs.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)
MIL-100	1805	0.81
MIL-100-DPA	1558	0.68
MIL-100-ODPA	1331	0.63

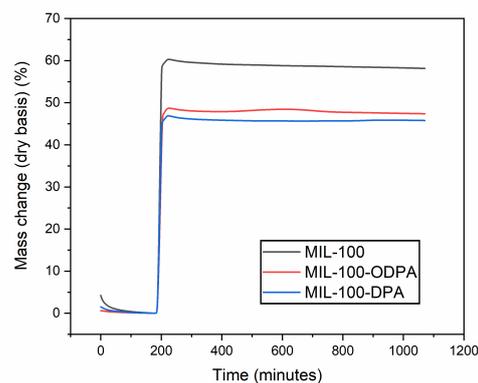


Figure 1: Toluene adsorption isotherms of the studied adsorbents at 95% P/P₀ toluene.

4 Conclusions

A facile hydrophobic surface modification method using two different alkyl phosphonic acids (DPA and ODPA) was applied to transform a hydrophilic and highly porous metal organic framework (MIL-100). The covalently integrated acids retained most of the inherent porosity and surface area of the pristine MOF. When the MOFs were tested for toluene removal, all samples demonstrated significant uptake quantities compared to a conventional activated carbon due to strong adsorbate-adsorbent interaction. However, a realistic assessment considering the co-existence of moisture must be performed to obtain the actual toluene removal performance. Developments are being done in our lab to optimize the coating methodology and to improve the toluene uptake amount further.

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6 References

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